

Temperature and Alkali Cation Dependency on the Memory Effect and Its Reconditioning Observed in Alkaline Secondary Batteries

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Introduction By repeating shallow discharging and overcharging of alkaline secondary batteries using a nickel electrode, a lowering of working voltage is observed on the discharge curve, which is called a memory effect. Results that the formation of -NiOOH appears to be the main cause of the memory effect^{1, 2)}. In the present paper, we studied how the temperature change and the cation species affect the memory effect and reconditioning.

Experimental The positive capacity-limited cell with about 75 mAh was fabricated using a nickel and a cadmium electrode obtained from a commercially available battery. This cell was soaked and tested in an 8 M KOH solution. Cycling with a charging current of 20 mA (3.2 mA/cm²) for 5 h and at the same discharging current to a 1.2 V cutoff voltage was conducted for appropriate cycles to produce a memory effect (shallow discharge cycling) at various temperatures. After repeating the given shallow discharge cycling, the cell was discharged at 20 mA (3.2 mA/cm²) to a 0.8 V cutoff voltage at 30 to examine the effect of the preceding shallow discharge cycles. Reconditioning was carried out in an 8 M alkaline solution while changing the concentration of KOH and NaOH ratio.

Results and Discussion Figure 1 shows the discharge time at 30 after 20 cycle shallow discharge cycling carried out at various temperatures and the capacity retention rate (= discharge time to 1.2 or 0.8 V at 30 after shallow discharge cycling at various temperatures / discharge time to 1.2 or 0.8 V of a normal cell at 30) at various temperatures. This figure shows that discharge time to 1.2 V increases and that the time to 0.8 V increases as the shallow discharge cycling temperature drops. The capacity retention ratio at the 1.2 V

cutoff voltage may be an indicator for the memory effect, which decreased to 35 of the charged state Ni electrode after 20 cycle shallow discharge cycling at various temperatures indicates that diffraction peaks due to -NiOOH appear more clearly for the Ni-electrode depending on the quantity of -NiOOH, when shallow discharge cycling was carried out at lower temperatures (Fig. 2). The oxidation number of -NiOOH is 3-3.2, while that of -NiOOH is about 3.7. This suggests that the latter NiOOH has a larger capacity, which is reflected in Fig. 1, i.e., the discharge time to 0.8 V is longer for the electrode when shallow discharge cycling was carried out at lower temperatures. These results confirm that the cause of the memory effect is mainly due to the formation of -NiOOH. The memory effect was tended to occur in a NaOH solution more than in a KOH solution. The reconditioning effect, i.e., the degree of recovery of the memory effect as a result of deep charge-discharge cyclings was also higher in a KOH solution than in a NaOH solution.

References 1) Y. Sato, S. Takeuchi, S. Magaino, and K. Kobayakawa, Bull. Chem. Soc. Jpn., 73, 1699 (2000). 2) Y. Sato, S. Takeuchi, and K. Kobayakawa, Electrochim. Acta, 93, 20 (2001).